



Review

Simultaneous oxidation of carbon black and volatile organic compounds over Ru/CeO₂ catalystsSamer Aouad¹, Edmond Abi-Aad*, Antoine Aboukais

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ARTICLE INFO

Article history:

Received 7 July 2008

Received in revised form 2 October 2008

Accepted 8 October 2008

Available online 15 October 2008

Keywords:

Carbon black

Catalysts

Ruthenium

TPR

XRD

VOC

ABSTRACT

Ru/CeO₂ catalysts with Ru loading of 1–5 wt.% were prepared by wet impregnation from aqueous ruthenium (III) nitrosyl nitrate solution and activation with an air flow at 600 °C for 4 h. This activation resulted in a considerable reactivity for the catalytic oxidation of carbon black (CB) ($T_{50\%} \sim 350$ °C “tight contact” mixtures and $T_{50\%} \sim 515$ °C “loose contact” mixtures) and volatile organic compounds (VOCs) ($T_{50\%} = 175$ °C for propene, $T_{50\%} = 215$ °C for toluene). When carbon black oxidation was conducted under “propene (6000 ppm) + air” or “toluene (2000 ppm) + air” flow, the elimination of an important part of CB was observed at relatively low temperatures comparing to its elimination under pure air flow. These temperatures correspond to the total oxidation of the VOC present in the reactant gases. Carbon black total elimination was also investigated under isotherm conditions in the presence and in the absence of propene. Total elimination occurred during shorter times when combustion was performed under propene. TPR study showed that ruthenium species present in the catalysts after activation reduces at relatively low temperatures (<100 °C) and that from a Ru loading of 1.5 wt.%, agglomerated ruthenium oxide was formed and that this latter is more difficult to reduce (>100 °C).

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1. Introduction

Reducing the particulate matter (PM) and volatile organic compounds (VOCs) emissions simultaneously has been a major challenge for car manufacturers and researchers. In fact, in several cases, VOCs emissions are accompanied by carbon particulates emissions. The most known example is that of diesel engines [1–3], but many industries are also sources of particulate and volatile emissions [4]. Emission control strategies include changes and improvements in the fuel used, engine or process modifications or exhaust after-treatment systems. These latter provide satisfactory results for compliance with the emission regulations where the engine or process modifications or fuel improvements are not sufficient. Using oxidation catalysts in order to oxidize carbonaceous particulates is one of the promising after-treatment systems. These catalysts also provide significant reductions in the carbon monoxide (CO) and hydrocarbons (HC) emissions.

In literature, different laboratory experiments were performed to study the combustion of soot particulates. In some of it, carbon black (CB) oxidation was studied under isothermal conditions and in others “CB + catalyst” mixtures were subjected to a dynamic temperature increase. Reactant gases ranged from synthetic air [5] to mixtures of different gases “O₂, NO, H₂O, SO₂, N₂...” [6,7].

Ruthenium oxide catalysts have been demonstrated to be reactive in acetic acid [8], propene [9] and carbon black [10,11] oxidation reactions. The pronounced reactivity of ruthenium oxide catalysts seems to result from the reducibility of the oxide itself. In the presence of another reducible oxide such as ceria (CeO₂), the oxygen needed for the oxidation reaction was reported to be provided by the second oxide.

In this paper, the simultaneous oxidation of carbon black and volatile organic compounds over Ru/CeO₂ catalysts is investigated.

2. Experimental

2.1. Synthesis of Ru/CeO₂ catalysts

Cerium hydroxide Ce(OH)₄ was precipitated from cerium (III) nitrate hexahydrated solution Ce(NO₃)₃·6H₂O 0.25 M and a sodium hydroxide alkali solution NaOH 1 M. The resulting hydroxide Ce(OH)₄ was filtered, washed and dried overnight in a drying oven at 100 °C, then it was calcined at 500 °C to obtain ceria CeO₂. Different volumes of ruthenium (III) nitrosyl nitrate Ru(NO)(NO₃)₃ solution have been impregnated on ceria in order to obtain solids with different loadings of ruthenium (1, 1.5, 1.65, 1.85, 2, 3, 5 wt.%). These solids have been designated as RuxCe (x stands for the Ru wt.%). After drying at 100 °C for about 20 h, they were stabilized by calcination under dried air at 600 °C for 4 h.

2.2. Catalytic tests

The catalytic test towards the combustion of carbon black (CB) (N330 DEGUSSA: specific surface area $S_{sp} = 76 \text{ m}^2 \text{ g}^{-1}$, elementary analysis: 97.23 wt.% C; 0.73 wt.% H; 1.16 wt.% O; 0.19 wt.% N; 0.45 wt.% S) was studied by simultaneous thermogravimetric (TG) – differential scanning calorimetry (DSC) analysis with NETZSCH STA 409 apparatus. Before test, 10 wt.% of CB and 90 wt.% of catalyst were mixed slightly in an appropriate cell for 10 min (“loose contact”) or heavily in a ball miller for 40 min (“tight contact”). Thirty milligrams of the mixture were then loaded in an alumina crucible and heated from room temperature up to 1000 °C (5 °C min^{−1}) under air flow of 75 mL min^{−1}.

The propene (C₃H₆; 6000 ppm) and toluene (C₇H₈; 2000 ppm) oxidations were carried out in a catalytic micro-reactor coupled to a

Varian 3600 gas chromatograph using a double detection FID and TCD. Hundred milligrams of the catalyst were tested in the presence of the different VOCs (air + VOC = 100 mL min^{−1} – 1 °C min^{−1}).

The propene/toluene and carbon black simultaneous oxidation was studied using the previous two techniques. Concerning DSC/TG technique, the experimental design was kept unchanged but a fixed amount of propene was introduced into reactant gases flow. The total flow was also increased from 75 mL min^{−1} to 100 mL min^{−1} for comparison reasons. The second technique coupled a catalytic micro-reactor to a Varian 4900 micro-gas chromatograph. This latter allowed consecutive automatic injections separated by relatively short time periods (120 s for propene test and 90 s for toluene test). Thus, several points corresponding to the combustion of carbon black in the presence of a VOC were recorded. Hundred milligrams of the catalyst mixed to 10 wt.% of CB were tested in the presence of propene/toluene (air + propene = 100 mL min^{−1}; 6000 ppm of propene or air + toluene = 100 mL min^{−1}; 2000 ppm of toluene – 1 °C min^{−1}). For isothermal studies, catalyst/CB mixtures were heated from room temperature till the isotherm temperature (1 °C min^{−1}). Initial time ($t = 0$) corresponds to the beginning of heating under reactant gases flow. Thus CB conversion begins before the isotherm settlement. The micro-reactor is loaded with a 111 mg of the mixture in a way to have a constant catalyst quantity (100 mg). After reaching the desired isotherm duration, the micro-reactor is rapidly cooled (to stop the reaction) and the recovered mixture is analysed by TG apparatus to determine remaining CB quantity.

2.3. Characterization of the solids

2.3.1. BET and elemental analysis

The specific surface areas (S_{sp}) were measured based on BET method using an ANKERSMIT Quanta Sorb Junior apparatus. Calcined samples are treated at 130 °C under nitrogen flow for 15 min. The adsorption of a “30% N₂ (adsorbed gas) + 70% He (carrier gas)” mixture is then carried at −196 °C. After the completion of adsorption, the sample is removed from liquid nitrogen and leaved at room temperature. This quick heating of the sample desorbs the gaseous nitrogen which is quantized using a thermal conductivity detector. Specific surface areas are given in Table 1.

Elementary analyses were performed on the calcined solids and element weight percentages are given in Table 1.

2.3.2. XRD analysis

The XRD experiments were performed at ambient temperature on a BRUKER D8 Advance diffractometer using CuK α radiation (1.5405 Å), which components are subtracted from the rough spectrum. The scattering intensities were measured over an angular range of $20^\circ < 2\theta < 60^\circ$ for all the samples with a step-size of (2θ) = 0.02°. The diffraction patterns have been indexed by comparison with the JCPDS files.

Table 1
Specific surface areas (S_{sp}) and elementary content (m%) of the solids.

Sample	S_{sp} (m ² g ^{−1})	Ru (m%)	Ce (m%)	O (m%)
CeO ₂	93	–	–	–
Ru0.67Ce	89	0.56	77.51	21.93
Ru1Ce	86	0.85	76.85	22.3
Ru1.5Ce	82	1.31	78.71	19.98
Ru2Ce	78	1.79	77.47	20.74
Ru3Ce	71	2.53	76.02	21.45
Ru5Ce	64	4.15	74.65	21.2
RuO ₂	45	–	–	–

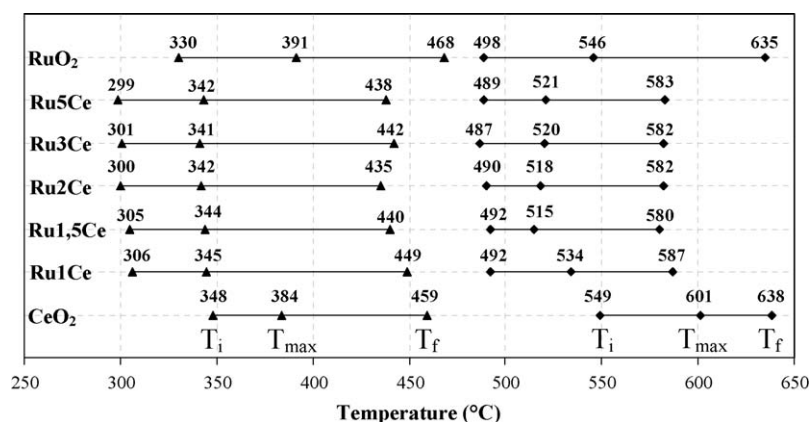


Fig. 1. Characteristic carbon black (10 wt.%) oxidation temperatures (◆) loosely or (▲) tightly mixed to different RuxCe catalysts.

2.3.3. TPR analysis

Temperature programmed reduction analysis (TPR) was carried out with a flow type reactor. Hydrogen (5 vol.% in Ar) was passed through a reaction tube containing the catalyst under atmospheric pressure at 30 mL min⁻¹. The tube was heated with an electric furnace at 5 °C min⁻¹, and the amount of H₂ consumed was monitored with a TC detector.

3. Results and discussion

3.1. Catalytic reactivity in CB oxidation

Catalytic reactivity in CB oxidation was determined by following the evolution of DSC curve, a technique in which the difference in energy input into our mixture and a reference material is measured as a function of temperature, while the mixture and the reference material are subjected to a controlled temperature program. The maximum of the DSC curve corresponds to the temperature of the highest rate of CB combustion, T_{\max} . In an earlier work [10], T_{\max} obtained for “20 wt.% CB + 80 wt.% catalyst” mixtures prepared under “loose contact” conditions were presented. Fig. 1 recapitulates T_i (CB oxidation ignition temperature), T_{\max} and T_f (end of weight loss) results for “10 wt.%CB + 90 wt.% catalysts” mixtures obtained under “loose contact” and “tight contact” conditions. Catalytic properties of solids are evaluated by comparing these temperatures with those of CB combustion without catalyst in the same conditions. The total combustion of CB without any catalyst was performed using SiC as an inactive support and has exhibited one exothermic peak with $T_i = 530$ °C, $T_{\max} = 629$ °C and $T_f = 635$ °C. It is observed that for “loose contact” mixtures, T_{\max} stabilizes for Ru contents ≥ 1.5 wt.%. This stabilization of the reactivity was already explained in our earlier work [11] using TPR results. In fact, it was shown that starting from a Ru content of approximately 1.5 wt.%, the surface of ceria is saturated with well dispersed ruthenium oxides, which causes cluster formation of these latter. One should note that RuO₂ alone showed good results under both contact types in CB oxidation. This is probably due to the reducibility and mobility of this oxide. Nevertheless, it remains less reactive than RuxCe catalysts. One should also notice that, due to different contact quality, T_{\max} decreases about 180 °C for the same mixture under different contact conditions.

In the aim of finding the optimum Ru content, two catalysts containing respectively 1.65 wt.% and 1.85 wt.% of Ru were synthesized. Fig. 2 shows TPR profiles obtained for freshly calcined catalysts containing respectively 1.5 wt.%, 1.65 wt.%, 1.85 wt.% and 2 wt.% of Ru. Starting from a 1.65 wt.% Ru content, a second

reduction peak appears at 129 °C. The intensity of this latter increased with the increase of ruthenium content. Simultaneously, the intensity of the first reduction peak decreases. Thus, this confirms and completes our earlier results [11] stating that the second peak corresponds to agglomerated ruthenium oxides. It is also evident that the formation of these agglomerated oxides induces a partial agglomeration of well dispersed ruthenium oxides interacting with ceria surface. Furthermore, when the two new catalysts were evaluated in the reaction of CB oxidation, the results were similar to those of Ru1.5Ce catalyst. It is then concluded that catalytic reactivity in CB oxidation is optimal for a Ru content equal to 1.5 wt.%. Therefore, most of the catalytic results throughout the manuscript correspond to the reactivity of Ru1.5Ce catalyst. Fig. 3 shows XRD patterns recorded for Ru5Ce catalyst freshly calcined at 600 °C and after different reduction steps: (A) before reduction, (B) after reduction at 95 °C and (C) after complete reduction at 250 °C. For all samples, the fluorite phase CeO₂ (JCPDS 65-2975 file) was observed. In fact, it was shown that during the heating of cerium hydroxide this latter dehydrates giving the oxide which crystallizes as CeO₂ [12]. This last presents diffraction peaks at 2θ equals 28.55°; 33.07°; 47.48°; 56.34° and 59.09°. In this structure, cerium atoms occupy a centered faces cubic lattice whereas the oxygen atoms are in tetrahedral sites. It is

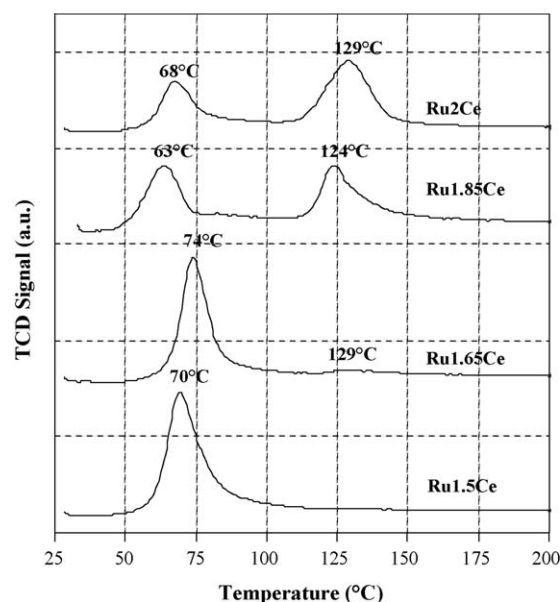


Fig. 2. TPR profiles of Ru1.5Ce, Ru1.65Ce, Ru1.85Ce and Ru2Ce catalysts.

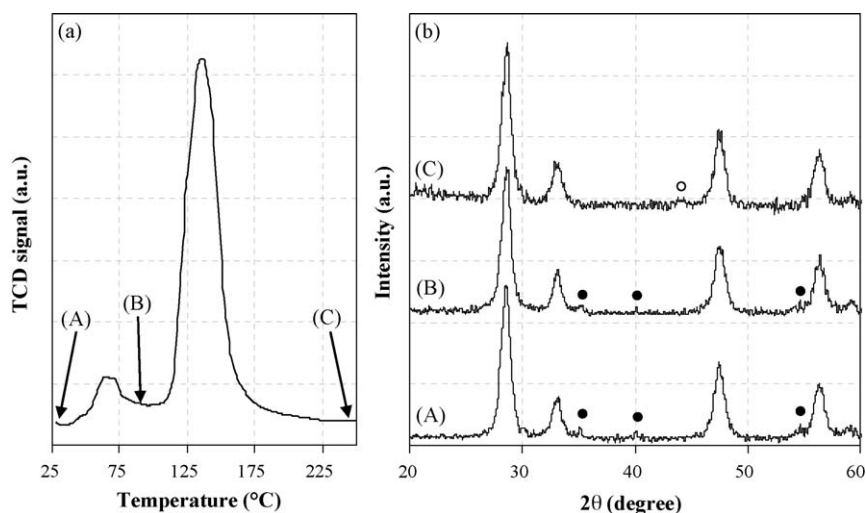


Fig. 3. (a) TPR profile of Ru5Ce calcined at 600 °C and (b) XRD patterns corresponding to different reduction temperatures; ● RuO₂; ○ metallic Ru.

observed that after reduction at 250 °C (total reduction of ruthenium oxide species), an XRD peak corresponding to metallic ruthenium appeared at $2\theta = 44.07^\circ$. At point (B), peaks corresponding to RuO₂ phase (JCPDS 40-1290 file) are still observed. This indicates that Ru species, reduced before 95 °C (first TPR peak), are not agglomerated but contrarily they are well dispersed. Nevertheless, XRD peaks corresponding to RuO₂ are slightly smaller relatively to those obtained for the freshly calcined sample (A). This reveals a partial reduction of ruthenium oxide species responsible for the second TPR peak even though the reaction was stopped at point (B).

3.2. Catalytic reactivity in VOCs oxidation

In a previous work [11], the catalytic reactivity of RuxCe catalysts in the oxidation of some VOCs was studied. It was observed from light-off curves that $T_{50\%}$ (temperature corresponding to the 50% conversion of the VOC) for propene (6000 ppm), toluene (1800 ppm) and *o*-xylene (2000 ppm) conversion are respectively 175 °C, 215 °C and 230 °C over Ru1.5Ce catalysts [11]. Fig. 4 shows propene conversion versus temperature, in the absence of catalyst, in the presence of ceria, RuO₂ and over Ru1.5Ce. While propene oxidation didn't exceed 20% at 400 °C in the absence of catalyst, light-off curves of CeO₂, RuO₂ and Ru1Ce showed $T_{50\%} = 395^\circ\text{C}$, $T_{50\%} = 198^\circ\text{C}$ and $T_{50\%} = 175^\circ\text{C}$, respectively. Propene conversion over RuO₂ is achieved at about 200 °C which is relatively too low comparing to the oxidation of the same propene quantity over CeO₂. This is probably due to the easier reducibility

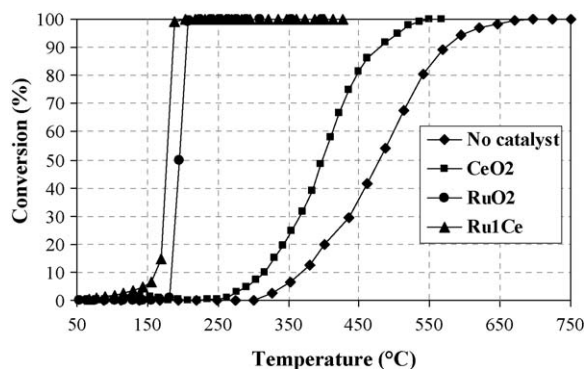


Fig. 4. Propene (6000 ppm) conversion as a function of temperature.

of RuO₂ compared to CeO₂. In fact, TPR profile of ceria shows two peaks at 500 °C and 797 °C (Fig. 5) corresponding respectively to surface and bulk cerium oxide reduction [13]. On the other hand, Fig. 5 shows that RuO₂ TPR profile exhibits two reduction peaks at 101 °C and 142 °C. In fact, the shape of RuO₂ TPR profile depends on sample mass. In the literature, it was reported that ruthenium oxide reduces in several steps ranging from 97 °C to 176 °C [14] or in one step at 110 °C [8]. Thus, RuO₂ is more reactive than CeO₂ due to its easier reducibility promoting a redox cycle which is favourable to the oxidation of propene in the presence of air. The addition of 1 wt.% of Ru to ceria made the oxidation of propene possible at a temperature lower than those obtained with each oxide alone (CeO₂ and RuO₂). Regardless of the good results obtained over RuO₂, the temperature drop (220 °C from 395 °C over ceria to 175 °C over Ru1Ce) is very important. In fact, ruthenium interacts with ceria, does not agglomerate for low contents and forms easily reducible species which are more reactive than RuO₂ alone. In addition, it is observed that the TPR peak corresponding to surface cerium oxide reduction is absent on Ru1Ce TPR profile (Fig. 5). In fact, after impregnation of the solution containing ruthenium on ceria, and during the calcination at 600 °C, oxygen bonds (Ru–O–Ce) are created between ruthenium and surface cerium. This oxygen, is weakly bounded, and readily reduces at temperatures ($\sim 70^\circ\text{C}$) lower than the temperatures

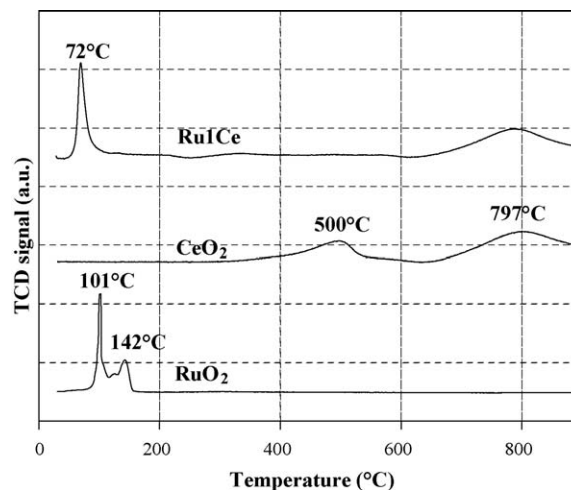


Fig. 5. TPR profiles of RuO₂, CeO₂ and Ru1Ce catalysts.

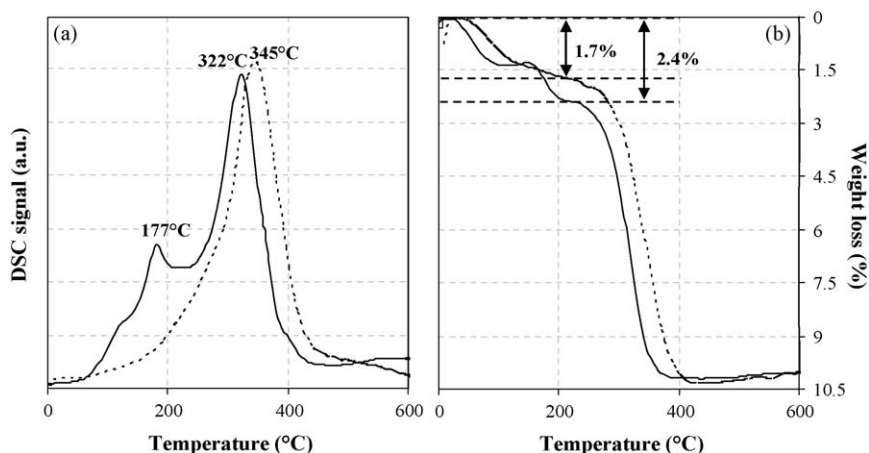


Fig. 6. (a) DSC and (b) TG curves obtained for “Ru1.5Ce + 10 wt.%CB” mixtures under “tight contact” conditions; under (---) air and (—) air containing 6000 ppm of propene.

encountered for pure ruthenium oxide (100–145 °C) and pure surface cerium oxide (350–600 °C). The catalytic reactivity of Ru/Ce catalysts in the oxidation of propene was not enhanced with the increase of ruthenium content [11]. As explained in the oxidation of CB, the increase of ruthenium content disables the interaction between all ruthenium oxide species and ceria surface inducing an agglomeration and an inhibition of the catalytic reactivity.

3.3. Catalytic reactivity in simultaneous CB and VOCs oxidation

After separately evaluating the reactivity of the catalysts in CB oxidation and VOCs oxidation [11], it was interesting to study their simultaneous oxidation over Ru/Ce. Results are presented separately depending on the type of contact for CB/catalyst mixtures.

3.3.1. “Tight contact”

Fig. 6 shows DSC/TG curves obtained for tightly mixed “Ru1.5Ce + 10 wt.%CB” mixtures under air or air containing 6000 ppm of propene. Fig. 6(a) shows two exothermic peaks under gas flow containing propene. The first peak at 177 °C is due to propene oxidation. A corresponding 2.4% weight loss (Fig. 6(b)) is observed between room temperature and the end of the first exothermic peak. Considering the TG curve obtained under pure air, the weight loss corresponding to the same temperature interval is only 1.7 wt.%. Thus, the exothermic peak at 177 °C corresponds not only to propene oxidation but also to the oxidation of a fraction of the CB present in the mixture. In addition, T_i for the mixture heated under air is equal to 305 °C whereas T_i corresponding to the second weight loss in the presence of propene is equal to 287 °C. A 23 °C difference is also observed between T_m obtained under air or air containing propene. The oxidation of all the initial quantity of CB (10 wt.%) is completed at 385 °C in the presence of propene and at 440 °C under pure air. Thus, the presence of propene in the reactant gases mixture is not only beneficial to the oxidation of a part of CB at low temperatures (~177 °C) but also to the faster completion of CB oxidation. Those observations are confirmed by a similar study realised in a micro-reactor in which the reactant gases mixture passes through the catalyst/CB mixture. Product gases are analysed using a micro gas chromatograph as explained in the experimental section. Fig. 7(a) and (b) show respectively the evolution of propene and toluene conversions and CO₂ quantity emitted during the oxidation of CB (Ru1.5Ce + 10 wt.%CB) under 100 mL min⁻¹ of air containing 6000 ppm of propene or 2000 ppm of toluene. A sharp and intense

CO₂ peak is observed at 179 °C for the reaction under propene and at 240 °C under toluene. CO₂ quantities that correspond to the total oxidation of propene or toluene are respectively equal to 1.8% and 1.4%. During the simultaneous oxidation, CO₂ quantity obtained at 179 °C under propene and 240 °C under toluene respectively is about 15%. From this observation one can conclude that CO₂ excess corresponds to the oxidation of a part of the CB present in the mixtures. It is known that VOC oxidation reactions are exothermic contributing to an increase of temperature as a result of heat production. This phenomenon is observed in our experiments especially on Fig. 7 where the shape of the CO₂ peaks shows clearly the rapid increase in temperature during VOC conversion (peak leaning to the right). A shift between reaction ignition and gases injection into the microGC makes the quantitative study of CO₂

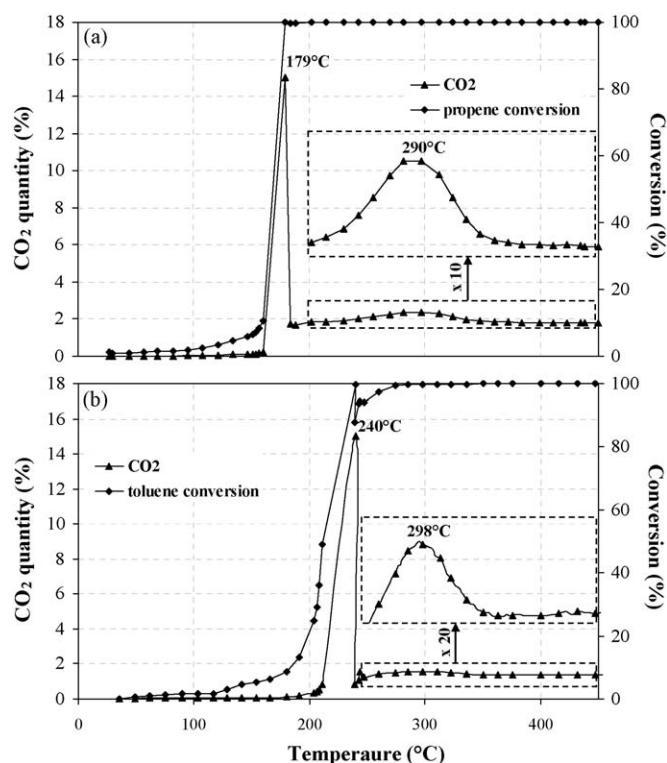


Fig. 7. VOC conversion and CO₂ quantity during the oxidation of “Ru1.5Ce + 10 wt.%CB – tight contact” mixtures under (a) 6000 ppm of propene and (b) 2000 ppm of toluene.

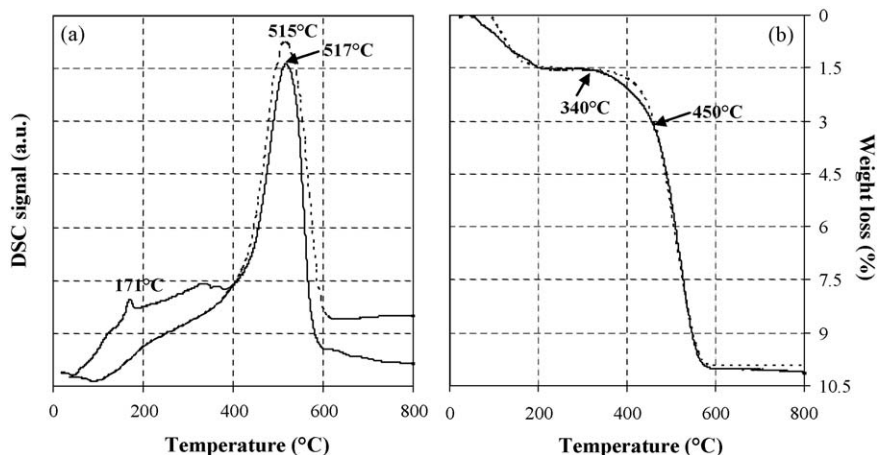


Fig. 8. (a) DSC and (b) TG curves obtained for “Ru1.5Ce + 10 wt.%CB” mixtures under “loose contact” conditions; under (---) air and (—) air containing 6000 ppm of propene.

very difficult and imprecise. After reaction ignition and VOC oxidation completion, CO₂ quantities fall down to 1.8% (propene) and 1.4% (toluene). However, a zooming of the 200–450 °C intervals on Fig. 7(a) and (b) shows a second exothermic peak. This latter indicates the oxidation of a remaining CB quantity even after the completion of VOC oxidation. It is important to note that the area of the second peak obtained at 290 °C under propene is twice more important than that of the second peak at 298 °C under toluene. This can be explained by the values of $T_{100\%}$ (temperature corresponding to the complete conversion of the VOC) obtained for the two VOCs. In fact, propene's $T_{100\%}$ (~180 °C) is lower than toluene's $T_{100\%}$ (~230 °C). Thus, this latter is closer to T_{\max} (344 °C) obtained for “Ru1.5Ce + 10 wt.%CB” mixture under pure air. It is then evident that, after reaction ignition and VOC oxidation, the CB quantity remaining inside the mixture is lower in the presence of toluene than in the presence of propene. At $T > 350$ °C in both reactions, CO₂ quantities stabilize at 1.4% and 1.8% in presence of toluene and propene, respectively. When we compare the temperatures in Fig. 7(a) to those obtained on DSC curve (Fig. 6(a)) for the same mixture under 6000 ppm of propene, we observe that the temperatures of the first peak are almost similar (177 °C and 179 °C for DSC and microGC analysis, respectively) while a ~30 °C difference exists between temperatures corresponding to the second exothermic peak (322 °C and 290 °C for DSC and microGC analysis, respectively). Thus, it seems that propene oxidation is not influenced by the way reactant gases contact the catalytic bed. This is not true for CB oxidation which occurs at lower temperatures when reactant gases flow goes through the catalytic bed (micro-reactor).

3.3.2. “Loose contact”

Under “loose contact” conditions, insignificant difference is observed between oxidation under pure air or air containing 6000 ppm of propene. Fig. 8 shows DSC/TG curves obtained for loosely mixed “Ru1.5Ce + 10 wt.%CB” under pure air or air containing 6000 ppm of propene. On the DSC curve obtained in air containing propene, an exothermic peak appears at 171 °C indicating propene oxidation. A second large exothermic peak (517 °C) is observed at almost the same temperature obtained under pure air (515 °C). Considering TG curves (Fig. 8(b)), the difference observed before 200 °C is due to different water and adsorbed gas quantities in each mixture. The two curves are perfectly superposed between 200 °C and 340 °C. At $T > 340$ °C, CB elimination is faster in the presence of propene. The two curves overlap again at 450 °C. Thus, propene exothermic oxidation makes CB elimination faster at 340 °C $< T < 450$ °C in the presence

of ruthenium based catalyst. However, the high reactivity of this latter in CB oxidation at $T > 450$ °C makes the exothermic effect of propene oxidation imperceptible. Fig. 9(a) and (b) show respectively the evolution of propene and toluene conversions and CO₂ quantity emitted during the oxidation of CB (Ru1.5Ce + 10 wt.%CB – “loose contact”) under 100 mL min⁻¹ of air containing 6000 ppm of propene or 2000 ppm of toluene. CB oxidation occurs at 475 °C in the presence of propene and also under toluene, which is 40 °C lower than T_{\max} obtained under pure air (Fig. 1). Propene conversion is completed before 200 °C with a corresponding CO₂ quantity of 1.8% (Fig. 9(a)). However, even after propene oxidation completion, CO₂ quantity continues to increase slightly (at

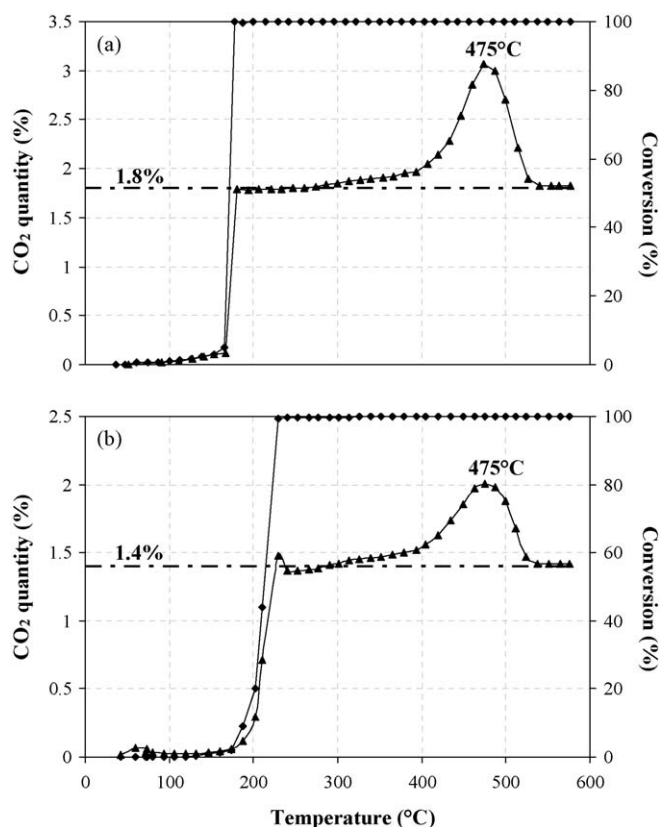


Fig. 9. VOC conversion and CO₂ quantity during the oxidation of “Ru1.5Ce + 10 wt.%CB – loose contact” mixtures under (a) 6000 ppm of propene and (b) 2000 ppm of toluene.

$T \geq 300^\circ\text{C}$) reaching a 3.1% peak at 475°C . This CO_2 excess corresponds to the oxidation of a part of CB present in the mixture. Thus, it appears that CB elimination begins at lower temperatures when propene is present in reactant gases mixture. Toluene conversion reaches 100% at $\sim 230^\circ\text{C}$ with a corresponding CO_2 quantity equal to 1.4% which continues to increase for $T \geq 300^\circ\text{C}$ and reaches a maximum of $\sim 2\%$ at 475°C (Fig. 9(b)). This maximum corresponds to the oxidation of CB present in the mixture. As the mixtures heated under air in the presence of propene or toluene contains initially similar CB quantities, corresponding CO_2 peaks should normally have equivalent areas. Nevertheless, Fig. 9 shows that CO_2 peak under propene is greater than the one obtained under toluene. This is due to hardware limitations. In fact, when the rate of CB elimination reaches its highest value ($\sim 475^\circ\text{C}$), CO_2 emission is maximal. If product gases injection into the microGC occurs just before or after maximum CO_2 emission, the corresponding point on CO_2 curve exhibits smaller height and consequently a narrower area. In addition, we already demonstrated that in the case of “tight contact” mixtures, a greater fraction of CB is eliminated under toluene. It seems that this is also true for “loose contact” mixtures. In fact, CO_2 emission in the presence of toluene exceeds 1.4% at 225°C . The excess corresponds to the elimination of a small quantity of CB. This was not observed in the presence of propene because its oxidation occurs at lower temperatures.

3.4. CB elimination in the presence of propene under isothermal conditions

In the perspective of a possible practical (industrial or mobile) application of our catalysts, elimination of CB in the presence of propene under isothermal conditions was realised.

3.4.1. “Tight contact”

Fig. 10 shows CB quantity evolution with time for “Ru1.5Ce + 10 wt.%CB” mixtures under different gaseous reactant flows and for different constant temperatures (a) 200°C and (b) 250°C . Two experiments were performed: the first with mixtures heated at 200°C or 250°C under 100 ml min^{-1} of pure air and the second with similar mixtures treated at the same temperatures under 100 ml min^{-1} of air containing 6000 ppm of propene. Fig. 10(a) shows that CB complete elimination is achieved after 8 h at 200°C under air containing propene. The rate of CB elimination calculated between the beginning and the

end of the isotherm is equal to $8.5\text{ mg}_{\text{CB}}\text{ g}_{\text{cat}}^{-1}\text{ h}^{-1}$. This value is about 4.5 times greater than the rate of CB elimination at the same temperature in the absence of propene ($1.9\text{ mg}_{\text{CB}}\text{ g}_{\text{cat}}^{-1}\text{ h}^{-1}$). Moreover, after 8 h at 200°C under air, 83% of the initial CB quantity is still present in the mixture. The difference between the rates ratio and the remaining CB quantities ratio is evident. In fact, the shape of CB (%) curve under propene shows a sharp weight loss between room temperature and 200°C . This latter is equal to 36% of the initial CB quantity. It is due to the ignition of propene exothermic oxidation which induces the elimination of an important part of CB present in the mixture. This is in agreement with DSC/TG results for the same mixture. In fact, Fig. 6(b) shows a weight loss at 177°C under propene attributed to the elimination of a CB fraction. This weight loss is lower than 36% of the initial CB quantity due to the quality of the contact between reactant gases and catalytic bed. Fig. 10(b) shows isotherms obtained at 250°C . The difference between CB elimination rates is less expressed at this temperature ($9.1\text{ mg}_{\text{CB}}\text{ g}_{\text{cat}}^{-1}\text{ h}^{-1}$ under air and $13.2\text{ mg}_{\text{CB}}\text{ g}_{\text{cat}}^{-1}\text{ h}^{-1}$ under propene). This is due to the higher value of the temperature (closer to $T_{\text{max}} = 344^\circ\text{C}$ obtained in DSC) and thus a higher catalytic reactivity. On the other hand, to calculate the rates, $t = 0$ was considered as the temperature of the beginning of the isotherm (250°C). At this time, CB quantities remaining in the mixtures are different (5.28 mg under propene and 9.9 mg under pure air) which influences the rates of reaction.

3.4.2. “Loose contact”

Fig. 11 shows CB quantity evolution with time for “Ru1.5Ce + 10 wt.%CB” mixtures under different gaseous reactant flows and for different constant temperatures (a) 400°C and (b) 450°C . Two experiments were performed: the first with mixtures heated at 400°C or 450°C under 100 ml min^{-1} of pure air and the second with similar mixtures treated at the same temperatures under 100 ml min^{-1} of air containing 6000 ppm of propene. At 400°C , CB complete elimination occurs after 10 h under propene while 37% of initial CB remains after the same duration under pure air. To complete CB elimination under air, it was necessary to keep the isotherm running for an additional 10 h. Thus propene presence contributes to CB complete elimination during time period twice shorter than that needed in its absence at relatively low temperature (400°C). Considering 10 h of isotherm, the rates of CB elimination are respectively equal to $8.4\text{ mg}_{\text{CB}}\text{ g}_{\text{cat}}^{-1}\text{ h}^{-1}$ and

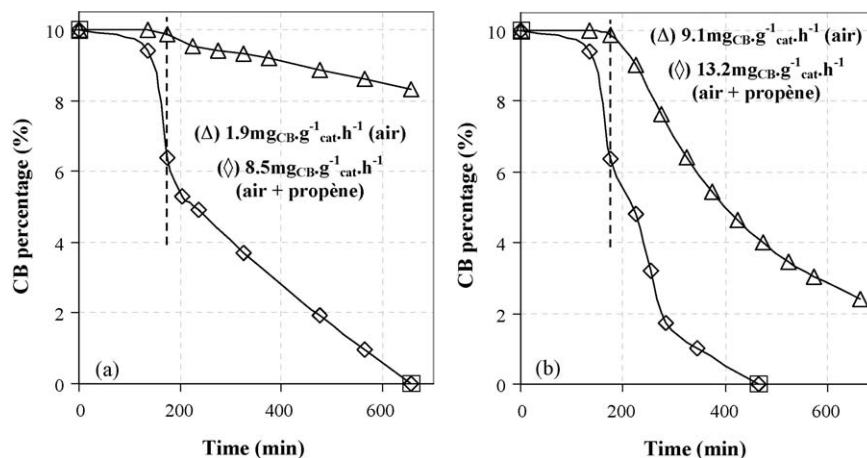


Fig. 10. CB quantity evolution in “Ru1.5Ce + 10 wt.%CB – tight contact” mixtures as a function of isotherm time under (Δ) air and (◇) air containing 6000 ppm of propene at (a) 200°C and (b) 250°C .

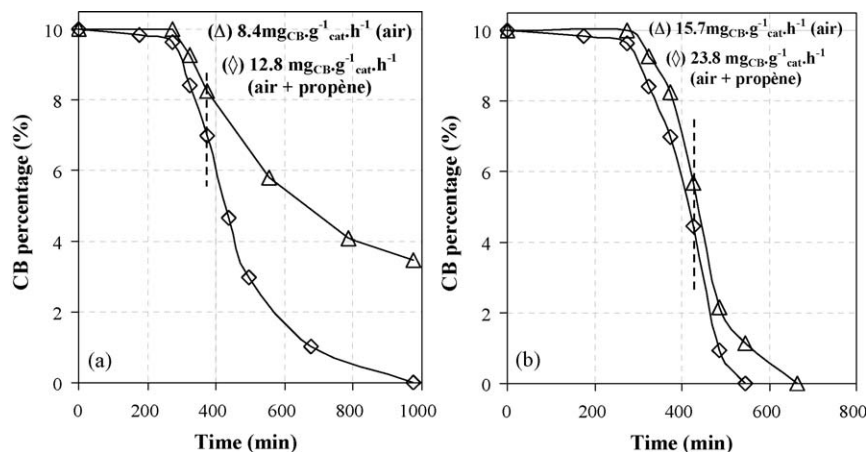


Fig. 11. CB quantity evolution in "Ru1.5Ce + 10 wt.%CB – loose contact" mixtures as a function of isotherm time under (Δ) air and (\diamond) air containing 6000 ppm of propene at (a) 400 °C and (b) 450 °C.

$12.8 \text{ mg}_{\text{CB}} \text{ g}^{-1}_{\text{cat}} \text{ h}^{-1}$ under pure air and under air containing 6000 ppm of propene. This implicates that CB elimination is about 1.5 faster under propene at 400 °C. However, if we consider that CB is completely oxidized after 20 h under pure air, the corresponding rate will be equal to $4.5 \text{ mg}_{\text{CB}} \text{ g}^{-1}_{\text{cat}} \text{ h}^{-1}$ almost 2.8 times slower than in the presence of propene. This difference is due to slower kinetics when CB quantity in the mixture decreases.

When isotherm temperature is increased to 450 °C, CB elimination rates increase. CB is eliminated after 2 h under propene and it took 4 h to eliminate the same quantity under pure air. Elimination rates are equal to $23.8 \text{ mg}_{\text{CB}} \text{ g}^{-1}_{\text{cat}} \text{ h}^{-1}$ and $15.7 \text{ mg}_{\text{CB}} \text{ g}^{-1}_{\text{cat}} \text{ h}^{-1}$ under air containing propene and pure air, respectively. The rates ratio is equal to 1.5 which is lower than the rates ratio at 400 °C (2.8). As explained for "tight contact" mixtures, catalytic reactivity of Ru catalysts is higher when isotherm temperature is closer to T_{max} obtained during CB oxidation in the presence of the same catalyst (515 °C). Thus, CB elimination is appreciable at this temperature even if gaseous reactant flow does not contain propene.

The average temperature in diesel engines exhaust varies between 150 °C and 500 °C [15] and between 300 °C and 400 °C during normal duty according to technologic guide at www.Dieselnet.com. It is important to note that the amount of soot emitted by a diesel engine varies between 0.035 g km^{-1} and 0.12 g km^{-1} . If we consider a vehicle at a speed of 90 km h^{-1} , it emits $3\text{--}11 \text{ g h}^{-1}$ of soot. Ru based catalysts prepared in this work allow the elimination of $\sim 13 \text{ mg}_{\text{CB}} \text{ g}^{-1}_{\text{cat}} \text{ h}^{-1}$ at 400 °C in the presence of a VOC. Thus, under the same conditions as in our test, 230 g of Ru1.5Ce allow the elimination of soot at a rate of 3 g h^{-1} and 850 g of the same catalyst will eliminate soot at 11 g h^{-1} . In general, VOC content in industrial effluents varies depending on the nature of industrial activity. Concerning diesel exhausts, VOC content is in general lower than 6000 ppm. Nevertheless, other gases, like CO, which oxidation is also exothermic are present and may enhance CB elimination at lower temperatures. If we consider CB oxidation in the presence of Ru catalysts without propene in reactant gases flow, 820 g of catalyst are sufficient to eliminate soot at 7 g h^{-1} (average rate of soot formation).

4. Conclusion

Contrarily to many oxidation catalysts, RuxCe solids appeared to be reactive in CB oxidation for both contact types "loose and tight". RuxCe catalysts are also very reactive in VOCs oxidation by contributing to 100% conversion of propene at $T < 200$ °C, and at temperatures lower than 250 °C for toluene. It is also shown that RuxCe catalysts are more reactive than CeO_2 and RuO_2 alone in oxidation reactions. The optimum Ru content was determined to be equal to 1.5 wt.%. For higher contents less reactive RuO_2 agglomerates on ceria surface. The presence of a VOC in reactant gases flow was shown to be beneficial to CB elimination in the presence of RuxCe catalysts. In fact, the catalyst developed in the laboratory allows the elimination of $8.4 \text{ mg}_{\text{CB}} \text{ g}^{-1}_{\text{cat}} \text{ h}^{-1}$ at 400 °C under pure air. The presence of 0.6% of propene in reactant gases mixture increases CB elimination rate to $\sim 13 \text{ mg}_{\text{CB}} \text{ g}^{-1}_{\text{cat}} \text{ h}^{-1}$. Thus, it is shown that under certain conditions, the use of our catalysts can be envisaged for practical de-pollution purposes.

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